PHYSICO-ORGANIC STUDIES OF LINSEED OIL DRIERS

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

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CRAYTON KNOX BLACK, B.A., M.Sc.

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ACKNOWLEDGEMENT

The author is greatly indebted to the two directors of this work, Dr. Wm. Lloyd Evans and Dr. W. G. France. Dr. Evans' direction and suggestions on the organic chemistry of the problem and Dr. France's direction of the physical chemistry has made this work possible.

INTRODUCTION

The literature of linseed oil chemistry in all its phases is rather limited. That portion of this literature which deals with colloid chemistry is extremely scant. Slansky[1]

1. Z. fur. Angew. Chem. p. 533 (1921)

put forward the view that polymerization of linseed oil is a colloidal phenomenon. Auer[2,3] believes that gas is absorbed

2. Koll. Z. 42, 288 (1925)
3. Koll. Beih. 24, 368 (1927)

after gelation and says that both phases of this iso-colloid are important. Long, Zimmerman and Nevins[4] have studied the

4. J. Ind. and Eng. Chem. 20, 806 (1928).

absorption of liquids by oil gels, while Clarke[5] finds that

5. Nature 120, 119 (1927).

these gels have a crystalline enough structure to give definite X-Ray patterns. From viscosity data Slansky and Kohler[6]

6. Koll. Zeit. 46, 128 (1928)

conclude that vegetable oils are dilute iso-colloids while mineral oils are not colloidal. All of these authors deal with iso colloids and gels.

Seaton and Sawyer[7] have studied the viscosity, not of

7. J. Ind. and Eng. Chem. 9, 35 (1917).

oils alone, but of varnishes, and they draw some very interesting conclusions, According to their work, colloid systems show straight line temperature - viscosity curves while true solutions give a curved line graph. They distinguish between colloidal varnishes and true solution varnishes. They find that colloidal varnishes, upon ageing, disperse into true solution systems, the viscosity becoming constant in about one month. A thinner also disperses the colloidal particles according to their data. Their systems included gums as well as driers which might be colloidally dispersed.

PROCEDURE

In this work, it was desired to study from a physical chemical point of view the action of driers in linseed oil systems.

Linseed oil is an extremely complex mixture. In order to simplify the problem and to reduce the number of variables involved, a system of simpler composition was used. Linseed oil is regarded as a mixture of triglycerides of oleic, linolic and linolenic acids as well as some saturated acids. The use of the individual triglycerides of these acids would greatly simplify the system and in this work that of oleic acid or olein was used as the medium.

Olein was prepared by the method of Belluci and Manzetti[8] as follows: Stoichiometric amounts of C.P. oleic

8. C, p. 1047 I (1911).

acid and glycerine were heated in a vacuum to 260°C. The water which split off was removed by suction and an oily product of a rather high degree of purity was obtained. It was dried over calcium chloride in a vacuum. Its freezing point was -6°C. and its density .91 which is in good agreement with the literature[9]. The acid value was 3 and the iodine value 85.

9. Lewkowitch - Chem. Tech. and Analysis of Oils, Fats and Waxes, Vol. III).

Conclusion

The color was pale yellow. While obviously not of 100% purity it was believed to be satisfactory for this investigation. Olein does not dry to a hard film on exposure to air as does linseed oil, so that when drying tests were made, linseed oil, was substituted. The metals commonly used as driers, namely lead, manganese, and cobalt were made up as cleates. Zinc oleate as an example of a poorer drier was also prepared. The following procedure was used in making these oleates. Sodium oleate C.P. was dissolved in water and a solution of a salt of the metal added to the oleate with rapid stirring. The metallic oleate, which precipitated, was filtered, washed until free from the anion and dried in a vacuum. The precipitating solutions were cobalt chloride, manganese sulfate, lead acetate and zinc sulfate. The cobalt oleate was a purple granular material which rapidly oxidized in air to a black hard mass (Compare C I 1040 (1902)). The manganese oleate was very nearly white and rather granular (A 244, 266). The lead oleate was a white sticky mass which dried to a substance of resinous character (A.57 45). The zinc oleate was very white and powdery (Gm 4 1494).

These oleates were analyzed for metallic content and found to be of practically theoretical purity.

Solutions of oleates in olein of .04 molar concentration were used. This approximates rather closely a 1% solution, The oleate was weighed out, the olein added and the beaker heated in a water bath to 100°C until solution appeared complete which was usually 20 to 30 minutes. When solutions of different

oleates were made up for comparison all were heated at once in the same water bath, so that the treatment would be exactly the same. In this way a system is produced in which the oleic acid radical is alone and not influenced by quantities of other organic chains.

In an attempt to relate some physical property with drying power, refractive indices and surface tensions were both measured. The values obtained for these systems showed such small differences, when compared with each other that no definite conclusions were warranted.

An interesting observation was made when it was found that the quantity of precipitate which had settled out of these systems was inversely proportional to the drying power of the metal oleate. The cobalt system had practically no precipitate, the manganese but very little more, while the lead system showed an appreciable precipitate. The zinc system was a pasty mass throughout with very little fluidity. This order coincides with the order of drying power of these metals as given by Fokin[10] and others, namely cobalt, manganese, lead and zinc.

10. Seif. Zeit. 34, 821

With the thought in mind that solubility might be an important factor in drying power the following experiment was carried out. Finely divided lead is known to increase the rate of drying of linseed oil. In this case the four metals mentioned above finely divided (passed 150 mesh and retained

on 200 mesh screen) were shaken up in linseed oil to give systems of equal concentration of metal. The drying time for these oils was observed and the following drying order found; lead, manganese, cobalt, and zinc. This is a variation from the usual drying order. The undissolved metal was then recovered in each case and the solubility of the metal in the oil calculated. The solubilities were found to fall in the same order, lead being the most soluble. The amount of metal dissolved in 100 cc. of oil is given below.

Pb - .0333 g.
Mn - .00425 g.
Co - .00368 g.
Zn - negligible

These data lead to the conclusion that the material in solution influences drying to a considerable extent and that therefore the solubility of the drier is a rather important factor.

Ultramicroscopic Examination.

The solutions were next viewed under a Siedentopf Cardioid Ultramicroscope using a direct current arc lamp as a source of light. In this microscope a very thin layer of the material is viewed in a quartz chamber. Photographs were made in each case with an "Aufsatz Microkamera" using 45 x 60 mm. plates.

The freshly prepared systems showed a rather high colloidal content. The particles exhibited an appreciable Brownian Movement although the displacements were rather small due presumably to the high viscosity of the medium. They exhibited distinct cataphoretic movement under a potential gradient of about 1000 volts per cm and were negatively charged. In a typical .04 molar cobalt oleate in olein system, freshly prepared, the particles appear rather small but are very numerous. The manganese system contains particles larger in appearance but fewer in number than the cobalt. The lead system, shows particles more massive in appearance than either cobalt or manganese. The .04 molar zinc oleate system contains no particles of colloidal dimensions. The colloidal content of all systems decreased materially with time becoming constant and practically negligible in about one month. Linseed oil systems made up from a good grade of oil of the following constants:

Iodine value --------	180
Acid value --------	2.2
Saponification value -	190

in which metallic linoleates, made in a similar way to the oleates, were dispersed showed systems of very great similarity to the oleate systems. It was found on drying these linseed oil systems that very little if any change in the dispersity of the colloidal content occurred during drying. Pictures taken of the dried oils can scarcely be distinguished from

those of the solutions, except in the case of lead. With a dried film containing lead as a drier, myriads of very tiny dots appear in the ultramicroscope, these dots occurring throughout the entire mass in addition to the larger colloidal aggregates of lead drier.

Previous work in this laboratory had pointed toward the fact that in linseed oil systems small amounts of cobalt salts added to a lead drier solution had the effect of dispersing the lead, With this in mind solutions were made up containing respectively .04, .02 and .01 gram mols of lead oleate per liter of olein. Before any settling occurred a portion of each of these solutions was put aside and enough cobalt oleate added to the rest of each solution to give a .02 molar cobalt solution. In each case after settling had occurred the amount of precipitate in the solutions containing cobalt as well as lead was very much less than in the corresponding solutions containing lead alone. For example the .04 molar lead solution had probably 3 or 4 times as much precipitate as the .04 molar lead + .02 molar cobalt. This same ratio of the quantity of precipitate holds even after a year of ageing. A study of the colloidal condition of these systems was deemed advisable. Immediately after preparation the system containing cobalt as well as lead shows a much greater number of particles than the lead alone due probably to the cobalt as well as the lead being

colloidally dispersed. After an ageing period in which settling out will occur, however, the solution containing lead and cobalt shows fewer particles than the lead alone. The disappearance of colloids occurs much sooner in the mixture than in the lead alone. Since the quantity of precipitate is less and the number of colloidal particles less with cobalt present it seems that the cobalt is dispersing the lead into true solution or at least into a state of subdivision, not detected by the ultramicroscope.

This dispersion of one soap by another is an interesting phenomenon and other combinations were tried. Because of the close relationship between cobalt, nickel and iron, it was decided to see if nickel and iron showed any dispersive action toward lead. In neither case did any very great dispersion occur although iron appeared a little more effective than nickel. Copper and manganese as examples of other driers were tried, being dispersed as oleates in a lead oleate solution as above. Copper showed no dispersive action, but manganese did show some. It was not nearly as pronounced in its action as cobalt but was better than iron. The possibility of cobalt dispersing other heavy metals suggested the experiment of combining cobalt oleate with a solution of Barium oleate in olein. The cobalt here did show considerable dispersing power but not as great as in the case of lead oleate.

This phenomenon is of course of great interest to the varnish maker where it has been observed that combinations of driers such as lead and cobalt or lead and manganese are very advantageous. This mechanism is extremely difficult to explain. Since solubility is so intimately related to dielectric constant data it was thought that possible the cobalt oleate changed the dielectric constant of the olein to such an extent as to make the lead oleate more soluble. Dielectric constant measurements were made on olein, solutions of oleates in olein and solutions of mixtures of oleates but no detectable differences could be observed with the apparatus used which was of the null point type. The dielectric constants of these materials are however extremely low, about 3, and a very slight change would amount to a rather high percentage change and might possibly influence the solubility to a considerable extent. Some possibility of detecting differences was indicated when it was found that cobalt particles showed more rapid cataphoretic movement in an electric field than did lead particles under the same conditions. This would indicate a greater potential difference between the cobalt particle and the olein than between the lead particle and olein which would of course relate to dielectric constants. Further work, particularly on getting particles of the same size for comparison must be done before any definite conclusions can be drawn. It was also thought possible to change the dielectric constant of olein by adulteration with other oils and observe some difference of dispersion. Olein and castor oil mixtures

and olein and mineral oil mixtures were made up so that each had the same iodine number. The dielectric constants differed by about only one unit however and no difference in dispersity was noted when the metallic oleates were added.

Other possible explanations of this dispersion of one metal by another might be based on chemical grounds. Cobalt which is an excellent oxidizing catalyst might oxidize the lead to a tetravalent state forming a lead tetraoleate which we should expect to be more soluble in olein than the bivalent oleate. Since the rules of organic solubility state that there is a tendency for like to dissolve like, $Pb(OOCC_{17}H_{33})_4$ should dissolve to a greater extent in olein than $Pb(OOCC_{17}H_{33})_2$. An attempt to make this tetravalent salt failed and the possibility was pursued no farther, There is some evidence of valence change when an olein solution of cobalt oleate is exposed to the air. The system, originally of extremely red tint turns to a rather distinct blue color which may indicate cobaltic compounds. On the other hand the cobalt might influence the medium itself so that more lead could be dissolved. Just how such changes would take place in closed vessels is rather hard to picture and harder to determine experimentally. The following experiment was undertaken in the hope of shedding some light on this mechanism but the interpretation is difficult. The amounts of precipitate in solutions of .04 lead oleate in olein subjected to the

following treatment, were observed.

(1) A solution of lead oleate in olein, made up as usual and the solution blown with air at a steady rate for 24 hours.

(2) A volume of olein blown with air for 24 hours and then used as the solvent in making a lead oleate solution of the same concentration as (1).

(3) A solution of lead oleate in olein as used in earlier experiments, without any blowing with air. The heat treatment was identical for all three. (1) and (3) had about the same amounts of precipitate which was normal for a lead system. (2) had practically no precipitate. This would indicate that possibly the medium is influenced but this of course is not conclusive.

To return to the subject of solubility in its relation to drying power, it was intimated above that possibly only the material in true solution influenced drying. By true solution is meant any state of subdivision below that which can be identified with the ultramicroscope. In other words the thought is that the material in colloidal suspension has very little influence on drying. To test this idea linseed oil systems had to be used of course and the following experiments were performed. A linseed oil system containing cobalt oleate as drier in concentration of .04 molar was made up. A portion of it was retained and the rest

centrifuged at a speed giving 480 times gravity for four hours. A sample of this was retained and the remainder centrifuged at a speed giving 1520 times gravity for three hours. These three solutions were then observed under the ultramicroscope. The uncentrifuged system contained many colloidal particles. The material centrifuged at the lower speed showed the removal of many of the particles while the third sample showed practically no colloidal particles after centrifuging at the higher speed. These three systems containing varying amounts of material colloidally dispersed but probably very nearly the same amount in true solution, all dried in exactly the same time. Several checks were made on the time until the material was dry to touch and no difference whatever could be detected. This would indicate that the material colloidally suspended influences drying very slightly if at all, but the material must be in true solution to really be effective. The colloidal particles may serve as a source of material going into true solution and therefore indirectly influence drying as will be discussed later under the subject of ageing.

Since gums are known to increase the drying time of varnishes it was thought that possibly the gums acted as a protective colloid forming a film around the colloidal drier particles and preventing them from going into true solution. The following gums were used, Cumar, Kauri, Congo, Beckacite and Rosin. The solutions were made up by melting the gum in a

copper beaker and adding oil at 200°C. and heating to 250°. In the solutions containing drier the drier was added to the oil before the oil was added to the gum. The drier solutions without gums used for comparison were given exactly the same heat treatment. The gum solutions in linseed oil alone showed practically no colloidal particles with the ultramicroscope. Upon the addition of driers, the characteristic drier dispersion was obtained. Upon ageing however these systems showed no more particles than a control system without gum. This would indicate that the gums do not keep the drier in colloidal suspension but probably retard drying due to some chemical action or some physical influence such as viscosity change, etc.

An attempt was made to find the relation between oxygen absorption and the amount of drier in true solution. A solution of lead linoleate in linseed oil was made up, the colloid particles centrifuged out and solutions made up to .04, .03 and .02, molar quantities per liter. The gain in weight method was used, which is obviously not free from error. The oil not only absorbs oxygen from the air but at the same time gives up volatile material as decomposition products. The gain in weight is of course the difference between these two processes and is far from the true oxygen absorption value. In this work however a comparison only was desired and it was felt that since the readings were made under the same conditions in every case comparable results would be obtained. The procedure was as follows: a microscope slide was carefully cleaned and weighed. About eight or ten drops of oil were

added and the slide tilted to allow the oil to run over the surface so that very nearly the same area was covered by oil in each case. The slide was then weighed again and kept under a large glass beaker to protect it from dust. Weighings were made every day and the gain in weight calculated as per cent of oil taken originally. Readings were taken even after the oil had set to a hard film. From the data obtained, it was shown that the rate of oxygen absorption as measured by gain in weight methods is proportional to the amount of dissolved drier.

Ageing.

Varnish makers have for years allowed varnishes to age before using. It was known that a better product was obtained but the reasons for this were practically unknown. There are of course changes in viscosity etc., which makes a varnish of better qualities but the reason for increased drying power of aged varnishes has indeed been obscure. The suggestion of Seaton and Sawyer (loc. cit.) in which they mention dispersion of colloids into true solution upon ageing is illuminating. In this investigation it has been shown by ultramicroscopic examination that the colloid content of all olein-oleate systems decreased materially upon ageing. Evidence has also been presented for believing that only the material in true solution is really effective as a drier. We might represent the transitions possible in the systems by the following scheme:

True solution $\rightleftharpoons$ Colloidal dispersion $\rightleftharpoons$ Coarse precipitate. The disappearance of the colloidal state may mean an increase in either material in true solution or in precipitate or both. Since ageing increases drying power it was suspected that the material in true solution was increasing and analyses to check this point were made on solutions of different age as follows. The system was centrifuged at a speed giving about 1520 times gravity for three hours. This was found sufficient to reduce the colloidal content to a practically negligible quantity. Analysis of the top layer in the centrifuge tube was then made by two schemes: first the method of Long and Egge[11] in which

11. J.Ind. and Eng. Chem. 20, 809 (1928).

the metal was precipitated out by means of thioglycollic acid, this precipitate was then ignited to get rid of organic matter and the residue treated with sulfuric acid and weighed as sulfate. The second method of analysis was to simply ignite until all the oil had burned away, treat the residue with sulfuric acid and weigh as sulfate. Closely agreeing results were obtained with the two methods. The results of the analyses are given in Table I.

TABLE I.

Lead oleate in olein. .04 molar or 8.28 g. Pb per liter	Cobalt oleate in olein .04 molar or 2.36 g. Co. per liter.	Manganese oleate in olein. .04 molar or 2.196 g.Mn per liter
1 day ; 7.43 g per 1.	1 day ; 2.14 g per 1.	1 day ; 1.26 g per 1.
35 days; 7.33 g " 1.	3 days; 2.17 g " "	14 days; 2.22 g " "
1-1/2 mo;7.14	11 days; 2.33	1-1/2 mo;2.10
3 mo. ; 6.88	28 days; 2.32	3 mo. ; 2.05
13 mo. ; 5.41	30 days; 2.31	13 mo. ; 1.64
	35 days; 2.33	
	13 mo. ; 2.28	

Zinc oleate in olein. .04 molar or 2.6148 g. Zn per liter.	Lead Linoleate in Linseed Oil .04 molar or 8.28 g. Pb per liter.
1 day ; .008 g. per 1.	2 days; 6.20 g. per 1.
1-1/2 mo;.01	2 mo. ; 6.45
13 mo. ; .105	3 mo. ; 6.54
	9 mo. ; 7.8

From these data it will be seen that with olein-oleate systems ageing increases the amount of material in true solution in the case of cobalt, manganese (though on prolonged ageing there is some precipitation) and zinc but in the case of lead there is a decrease in the quantity of drier in solution with

time. This case of lead settling out to such an extent as to decrease the amount in true solution at first seemed to be diametrically opposed to the predictions that had been made. A study of a linseed oil system gave illuminating results however. Analyses were made on a linseed oil system containing lead linoleate as drier and the amount in true solution was found to increase with time. The difference in amounts in solution with linseed oil and olein may be explained as follows: the settlings from linseed oil systems containing driers are known to consist largely of lead salts of saturated acids. The oleic acid group acts similarly in many ways to a saturated acid and probably lead oleate is rather insoluble in these media compared to lead salts of more unsaturated acids. Now in the lead oleate - olein system no change would be apt to occur except in the solubility of the lead oleate itself. In the linseed oil system the colloidal material probably goes both ways, some into true solution, some into the precipitate, so that both of these increase with decrease in colloidal content. The precipitate contains however the lead salts of the more saturated acids, including possibly some of the oleic, and this would leave the solution more unsaturated or a better drying system due to two causes;(1) some lead from the colloidal particles has gone into solution (2) many of the more saturated, non drying acids have been removed as lead soaps. Since the cobalt, soaps of saturated acid chains are not insoluble this settling does not occur and ageing merely

increases the amount in solution at the expense of the colloidally dispersed material. Manganese behaves somewhat like cobalt although there is a slight insolubility appearing upon extended ageing. Zinc oleate is so very insoluble even from the start that one should expect very little drying power from it.

Polymerization.

The difference between the action of heat and air on linseed oil has long been recognized. Chataway[12] summarizes

12. J. Soc. Chem. Ind. 47, 167 (1928).

the matter well when he says we have oxidation without higher temperatures and coagulation with the application of heat. There are several references in the literature as to the mechanism of this coagulation or polymerization. Salway[13], Slansky[14]

13. J. Soc. Chem. Ind. 324 T, (1920).
14. Z. Angew. Chem. 34, 533 (1921).

Morrell[15], Long and his associates[16] all have put forth theories

15. J. Soc. Chem. Ind. 34, 105 (1915).
16. J. Ind. and Eng. Chem. 19, 62 (1927); 19, 903 (1927).

as to this mechanism. Knight and Stamberger[17] have investigated

17. J. Chem. Soc. 2791 (1928).

the polymerization of olein with the addition of sulfur rather than oxygen. Clarke[18] has studied the X-Ray patterns of dried

18. loc. cit.

oil films but apparently no study of polymerization has been made with the ultramicroscope. It is known of course that a lead drier influencesdrying in a different way than cobalt for instance. Cobalt apparently speeds up oxidation and will form a skin of dried oil over the surface thus shutting out the oxygen from the body of the oil film. Lead driers on the other hand while slower in their action seem to "body" the oil throughout its entire mass and then set to a hard gel. It has been suspected that lead catalyses polymerization and Long and Smull[19] have studied molecular weight changes occurring with

19. Ind. and Eng. Chem. 17, 138 and 905 (1925).

different driers present. With cobalt and manganese there is only a slight increase due to the addition of oxygen but with lead the molecular weight increases materially indicating polymerization in this case.

It was observed as mentioned before that a dried oil containing lead drier showed myriads of very tiny dots under the ultramicroscope in addition to the regular colloidal dispersed lead. This same phenomenon of the myriads of tiny dots was shown in the case of a dried film of raw oil containing no drier at all. In some work in which linseed oil was

exposed to ultraviolet light the same effect was produced. To verify this the following experiment was performed. Raw linseed oil was observed with the ultramicroscope and found to be optically empty. The oil was then exposed in its quartz cell out of contact with air to ultraviolet light from a Cooper Hewitt mercury arc for 30 minutes and again observed with the ultramicroscope. The tiny points of light were extremely numerous throughout the entire field. Tung oil subjected to the same experiment showed some points of light before exposure but very many more after exposure. Ultraviolet light is known to polymerize oil[30] and it was thought that

30. Stutz - Ind. and Eng. Chem. 18, 1235 (1926)

possibly this characteristic phenomenon indicates polymerization. Morrell[31] states that acids retard polymerization. A little

21. Varnishes and Their Components.

acetic acid was added to the linseed oil before its half hour exposure to ultraviolet light and practically no dots of light appeared after exposure. Morrell[32] also states that there must

22. J. Soc. Chem. Ind. 34, 105 (1915).

be at least two pairs of double bonds present in the chain for polymerization to take place. According to this statement polymerization should not take place with olein. Olein, optically empty, was exposed in a quartz cell to ultraviolet light for

thirty minutes and upon observation with the ultramicroscope no change was observed from the condition before exposure. As to whether these molecules polymerize enough to be seen under the ultramicroscope is rather difficult to prove but the characteristic pattern occurs when polymerization is known to have taken place and fails to appear when polymerization has not taken place. It is possible that several molecules come together and are large enough and enough different in refractive index from the medium to be detected with the ultramicroscope. The pattern observed is similar in some respects to that of a gelatine gel and thus colloidal gelation and polymerization which are strongly suspected in linseed oil systems, may be detectable in this way.

In connection with the polymerization studies, observations were made with the ultramicroscope on boiled and blown oils. One sample of linseed oil was blown with air at room temperature for three days. Another sample was boiled with a stream of air flowing on the surface for one hour at 300°C. The third sample was boiled in a similar way but in an atmosphere of CO_2 rather than air. Upon ultramicroscopic examination the CO_2 boiled oil showed a few tiny particles. The air boiled oil showed more particles than the CO_2 boiled, while the sample blown three days showed about the same number of particles as the CO_2 boiled.

Oxygen absorption rates, as measured by gain in weight as above, were observed on (1) Linseed oil boiled 1 hour at 300°C. in a current of CO_2; (2) Linseed oil boiled 1 hour at 300°C. in a current of air and (3) Raw linseed oil.

The raw oil although drying last absorbs the most oxygen. The CO_2 boiled oil absorbs more oxygen than the air boiled but dries more slowly. If the final gel film is due to coagulation or polymerization of certain previously formed intermediate products, then some speculation occurs as to what these products are and how they are produced. Apparently heat or oxygen, either one may disrupt the molecule in some way to make a polymerizable substance. In the case of a raw oil film the first oxygen absorbed may form certain compounds which act as pre-gelation materials and later coagulate to form a solid gel like film. Some disruption apparently is brought about by heat in the absence of oxygen, whereby a product is obtained which will absorb oxygen more rapidly than the raw oil and set to a film. A combination of heat and oxygen seems to be particularly favorable for the formation of this pre-gel material and a hard film is obtained in even shorter time. Driers may speed this gel fore runner formation by their oxidizing power although the heat treatment during the incorporation of the drier must be considered as influencing the medium itself.

CONCLUSIONS AND SUMMARY.

From the above data, the conclusions may be briefly summarized.

Apparently only the drier in true solution catalyzes the drying reactions of linseed oil. Substances colloidally dispersed do not appear to act as a drier directly but may serve as a source of material going into true solution. The colloidal content of all systems of metallic oleates dispersed in olein, was high in freshly prepared systems. The colloidal content of all systems decreased upon ageing. In the case of a cobalt drier the particles are apparently dispersed into true solution. Manganese behaves similarly to cobalt. Lead oleate settles out of olein somewhat. Zinc oleate shows an extremely low solubility and no colloidal particles. Colloidal particles of lead linoleate in linseed oil may serve as a source of material for increase in both the amount in true solution and quantity of the precipitate. The amount of material in true solution increases with time in the case of cobalt, manganese and zinc systems in olein and lead linoleate in linseed oil. In the case of lead oleate in olein a decrease in amount of material in true solution, with time, was noted. Cobalt seems to act as a dispersing agent toward lead oleate causing an increase in the degree of dispersion of the lead compound in olein.

No change in dispersion of drier is noted upon the drying of a linseed oil film containing metallic oleates. It appears that the rate of oxygen absorption is proportional to

the amount of drier in true solution.

The possibility of detecting polymerization in oils by means of the ultramicroscope has been suggested. A very fine dotted structure seems to be characteristic of polymerized systems.

From these data it will appear that the colloidal chemistry problem in oil systems is indeed an important one. A great many other factors must be considered in studying these systems however and colloid chemistry alone will not answer all questions. The dispersion of drier, the drying of the film to a gel and the polymerization of the oil, are all colloidal problems of utmost importance.